

Chemical short range order obtained from the atomic pair distribution function

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Abstract. Many crystalline materials show chemical short range order and relaxation of neighboring atoms. Local structural information can be obtained by analyzing the atomic pair distribution function (PDF) obtained from powder diffraction data. In this paper, we present the successful extraction of chemical short range order parameters from the x-ray PDF of a quenched Cu₃Au sample.

Introduction

In many alloys the different atoms are not distributed randomly, but show chemical short range order (SRO). The only information that can be obtained from a routine crystallographic structure refinement based on Bragg intensities is the average occupancies of the different atomic sites. The chemical SRO shows up as diffuse scattering. This diffuse scattering, obtained from single crystal scattering experiments, can be analyzed and SRO parameters can be obtained. A summary of this method can be found e.g. in Cowley (1995). However, in some cases it might be impossible to grow single crystals or to obtain crystals of sufficient quality for single crystal diffuse scattering measurements. In these cases a viable alternative is the use of powder diffraction as we demonstrate in this paper. A recently emerging method to analyze the local structure based on the total scattering pattern from crystalline powder samples is the atomic pair distribution function (PDF) method. The PDF is obtained via Fourier transform from the scattering data containing both Bragg and diffuse scattering contributions. The PDF gives the probability to find an atom at a distance r from another atom, in other words it gives the bond length distribution of the material. This approach is long known in the field of studying short range order in liquids and glasses but has recently been applied to crystalline materials showing positional disorder (e.g. Egami (1998); Proffen et al. (1999); Peterson et al. (2001); Božin et al. (1999); Louca and Egami (1999); Petkov et al. (2000), for more general

information see Billinge (2001)). However, it has been unclear if the PDF would be sensitive enough to extract information about chemical ordering in perfectly crystalline materials. In a previous study (Proffen, 2000) we have used simulated data based on structures showing chemical SRO to test the ability of the PDF method to extract SRO parameters. Those tests were successful and showed that in principle such information can be extracted. In this paper we chose the system Cu₃Au to verify those findings using 'real' data. The chemical ordering in Cu₃Au has been studied for quite some time (e.g. Chen et al. (1970)). The structure of Cu₃Au is cubic. The system undergoes a chemical order-disorder phase transition at $T_c=394$ C°. Above T_c the two atom types are randomly distributed, below T_c copper atoms occupy the corners of the unit cell and gold occupies the face centers. This work should be seen as proof of principle and we concentrate on the simplest case comparing a quenched sample showing nearly random ordering of Cu and Au with the fully ordered case.

Experiment

Two samples were investigated: ordered and disordered Cu₃Au. Both were obtained from the same master alloy prepared by melting of 99.999 % Cu and Au under vacuum. The alloy was homogenized by annealing for 2 h at 1200 K. An ingot of the annealed master alloy was rapidly quenched down to room temperature resulting in disordered Cu₃Au. Another ingot was slowly cooled down and allowed to anneal for a week at 723 K. This allowed the material to reach an ordered state. Both samples were then filed into powder. The powder samples were carefully packed between Kapton foils to avoid texture formation and subjected to diffraction experiments using x-rays of energy 29.09 keV ($\lambda=0.4257\text{\AA}$). The measurements were carried out in symmetric transmission geometry at the beamline X7A of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. Scattered radiation was collected with an intrinsic germanium detector connected to a multichannel analyzer. Experimental powder diffraction patterns are shown in Fig. 1. These data were then normalized in elec-

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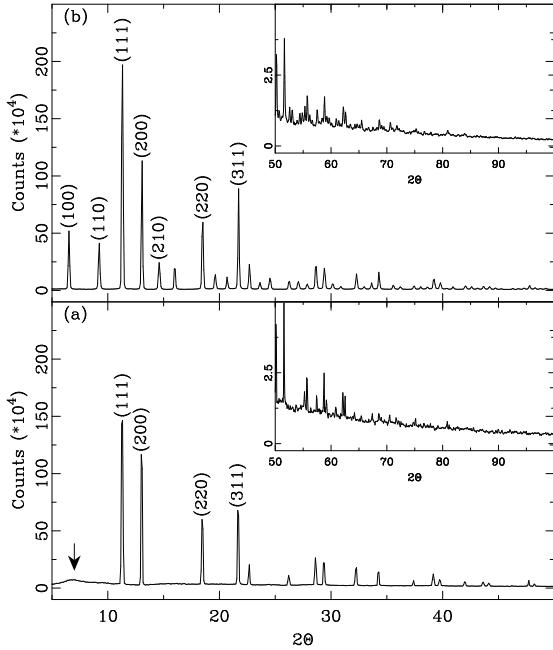


Fig. 1. Experimental X-ray powder diffraction data for (a) ordered Cu_3Au and (b) disordered Cu_3Au . Peaks are labelled with the corresponding Miller indexes.

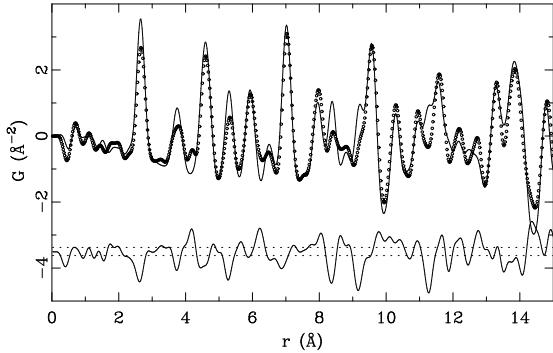


Fig. 2. Experimental PDFs from disordered (circles) and ordered (solid line) Cu_3Au . The difference is given below as solid line. The estimated experimental uncertainty is marked by horizontal broken lines.

tron units and converted to the structure functions $S(Q)$ (Klug and Alexander, 1974) after due correction for flux, background, Compton scattering, and absorption. The corresponding atomic pair distribution (PDF) functions, $G(r)$, are shown in Fig. 2. The data for both samples were terminated at $Q_{\text{max}} = 22.5\text{\AA}^{-1}$. All corrections and data processing was done with the help of the program *RAD* (Petkov, 1989). It is clear that, as well as the diffraction patterns, the PDFs of the ordered and disordered samples are significantly different.

Modelling and Results

Bragg peaks in the diffraction pattern of disordered Cu_3Au can be indexed with a cubic unit cell, space group $Fm\bar{3}m$. The ordered sample can be indexed in space group $Pm\bar{3}m$. The Miller indices (hkl) are shown in Fig. 1. One observes additional reflections for the ordered sample with mixed

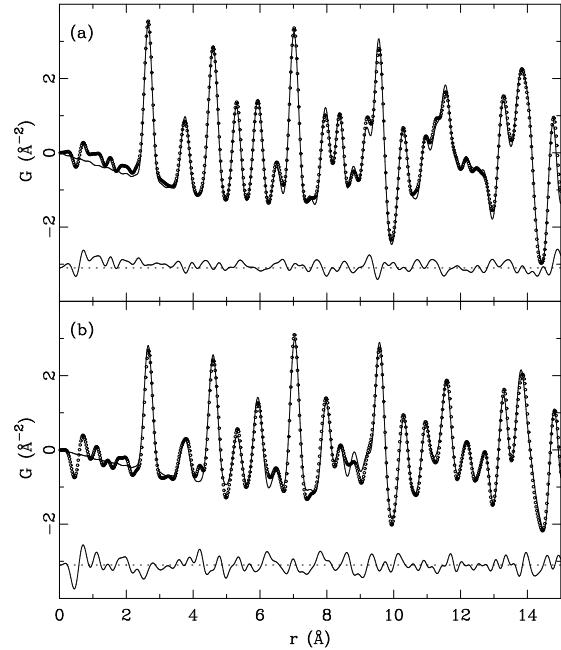


Fig. 3. Experimental (circles) and calculated (solid line) PDFs for the ordered Cu_3Au sample (a) and the disordered sample (b). The residual differences are shown below the data in both panels.

Table 1. Structural data of ordered and disordered Cu_3Au from PDF refinements. In the ordered case Cu is at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and Au is at $(0, 0, 0)$. For the disordered sample Cu and Au occupy both sites with an occupancy of 0.75 and 0.25, respectively. The units for the lattice parameters are \AA and for values of $\langle u^2 \rangle \text{\AA}^2$. The numbers in parentheses are the estimated standard deviation on the last digit. The weighted R-value R_{wp} corresponds to the refinement of the average structure, R_{wp} (RMC) corresponds to the result of the RMC refinement. For more details see text.

	ordered sample	disordered sample
a	3.75162(11)	3.7585(3)
$\langle u^2 \rangle (\text{Cu/Au})$	0.01307(2)/0.00772(3)	0.00939(4)
$R_{wp}/R_{wp}(\text{RMC})$	9.5/9.5	16.2/15.4

(odd + even) values of (hkl) . These reflections can be interpreted as super-lattice peaks showing up as a result of the ordering of copper and gold. The degree of order in the sample can be quantified by comparing the intensities of the super-lattice and fundamental Bragg peaks (Suryanarayana and Norton, 1998; Guinier, 1994). However, in cases where chemical SRO is confined to only a few nearest neighbors, one observes only broad diffuse scattering rather than sharp super-lattice peaks. A broad bump in the diffraction pattern at $2\Theta \approx 7^\circ$ marked by an arrow in Fig. 1a suggests the presence of SRO diffuse scattering. We chose to use the PDF technique to extract SRO parameters. The PDFs of the ordered and disordered sample are shown in Fig. 2. The PDF peaks for both samples are in nearly the same positions, since copper and gold are occupying the same cubic lattices. However, the intensity of the PDF peaks are different, since the PDF peak intensities are weighted by the respective scattering powers of the atoms contributing to that interatomic distance. Fig. 2 also shows that the difference is significantly larger than the experimental uncertainty shown as dashed lines.

The modelling of the PDF data is carried out in two steps:

First the PDFs are refined based on a model of the average crystal structure. In a second step Cu and Au are allowed to switch sites in a Reverse Monte Carlo (RMC) refinement (McGreevy and Pusztai, 1988) of a large model crystal. Chemical SRO parameters are then extracted from the final configuration of the RMC refinement.

The refinements of the average structure were carried out using the program *PDFFIT* (Proffen and Billinge, 1999). The refined PDFs are shown in Fig. 3. The only structural parameters refined are the lattice parameter and atomic displacement parameters for Cu and Au. These parameters are listed in Tab. 1. Details about the refinement procedure can be found in Proffen and Billinge (1999) and are not discussed here. The refinement extended over a range of $2.1 < r < 15.0$ Å. It is obvious from Fig. 3 as well as the weighted R values listed in Tab. 1 that the refinement corresponding to the random sample is not as good as for the ordered sample. When trying to refine site occupancies for the random sample, their values stayed at the expected 0.75/0.25 for Cu and Au respectively within one standard deviation. However, the worse R value as well as the modulated background of the scattering data for the random sample (Fig. 1), suggest some degree of chemical SRO present in the quenched sample, referred to as random in this paper. For the ordered sample, we observe no such indication.

The next step of the analysis are RMC refinements to allow Cu and Au to order locally. A comprehensive summary of the method applied to crystalline materials is given in Tucker et al. (2001). The algorithm works as follows: First, the PDF is calculated from the chosen crystal starting configuration and a goodness-of-fit parameter χ^2 is computed.

$$\chi^2 = \sum_{i=1}^N \frac{(G_e(r_i) - G_c(r_i))^2}{\sigma^2} \quad (1)$$

The sum is over all measured data points r_i , G_e stands for the experimental and G_c for the calculated PDF. The RMC simulation proceeds with the selection of a random site within the crystal. The system variables associated with this site, such as occupancy or displacement, are changed by a random amount, and then the model PDF and the goodness-of-fit parameter χ^2 are recalculated. The change $\Delta\chi^2$ of the goodness-of-fit χ^2 before and after the generated move is computed. Every move which improves the fit ($\Delta\chi^2 < 0$) is accepted. 'Bad' moves worsening the agreement between the observed and calculated PDF are accepted with a probability of $P = \exp(-\Delta\chi^2/2)$. For more details about the RMC refinement procedure used, the reader should refer to Proffen (2000) and the references therein. All RMC refinements were carried out using the program *DISCUS* (Proffen and Neder, 1997). We used a model crystal of 20x20x20 unit cells in size containing a total of 32000 atoms. The starting structure was given by the refinement result of the average structure (see Tab. 1). The only allowed RMC move was to have Cu and Au change sites. This way the overall concentration of Cu and Au was preserved. The refinement was aborted after 15 cycles when no further improvement in χ^2 was observed. A cycle is defined as the number of RMC moves required to visit every atom in the model crystal once on average.

To analyze the resulting structure after the RMC refine-

Table 2. Cu₃Au RMC refinement results. For details see text.

Neighbor	ordered sample		disordered sample	
	expected	RMC	expected	RMC
$\frac{1}{2}\frac{1}{2}0$	-0.33	-0.33	0.00	-0.10
100	1.00	1.00	0.00	0.19
$1\frac{1}{2}\frac{1}{2}$	-0.33	-0.33	0.00	-0.05
110	1.00	1.00	0.00	0.13
$\frac{3}{2}\frac{1}{2}0$	-0.33	-0.33	0.00	-0.10
111	1.00	1.00	0.00	0.05
$\frac{3}{2}1\frac{1}{2}$	-0.33	-0.33	0.00	-0.01
200	1.00	1.00	0.00	-0.08

ment is most convenient to describe the chemical SRO using correlation coefficients c_{ij} which are defined as:

$$c_{ij} = \frac{P_{ij} - \theta^2}{\theta(1 - \theta)} \quad (2)$$

P_{ij} is the joint probability that both sites i and j are occupied by the same atom type and θ is its overall occupancy. Negative values of c_{ij} correspond to situations where the two sites i and j tend to be occupied by *different* atom types while positive values indicate that sites i and j tend to be occupied by the *same* atom type. A correlation value of zero describes a random distribution. The maximum negative value of c_{ij} for a given concentration θ is $-\theta/(1 - \theta)$ ($P_{ij} = 0$), the maximum positive value is $+1$ ($P_{ij} = \theta$).

Table 2 lists the correlation parameters for the first eight neighboring shells for the ordered and disordered sample. The columns labelled 'expected' give the theoretical correlation parameters for the fully ordered or fully random case. The columns labelled 'RMC' list the resulting correlation coefficients of the RMC refinements. In case of the ordered sample, the RMC refinement was not able to find any configuration different from the fully ordered case that would lead to an improvement of χ^2 . As a result, the resulting correlation parameters are identical to the expected ones. In case of the random sample the situation is different, we observe values significantly different from zero which describes the fully random case. The weighted R value improved from 16.2% to 15.4% in the RMC refinement of the PDF from the random sample. Inspection of Tab. 2 shows that the chemical SRO found in the sample referred to as random is in fact of the same nature as in the ordered sample, i.e. nearest Cu-Cu and Au-Au neighbors are avoided and second nearest neighbors are preferred. However, for neighboring shells higher than five, the order is indeed random. In other words, locally Cu and Au atoms started ordering below the transition temperature, T_c , before being arrested by the rapid quench.

Conclusion

In an earlier paper (Proffen, 2000) we have shown that chemical SRO parameters can successfully be extracted from simulated data using the PDF analysis method. In this paper we have shown that chemical SRO parameters can also successfully be extracted from real data. The results

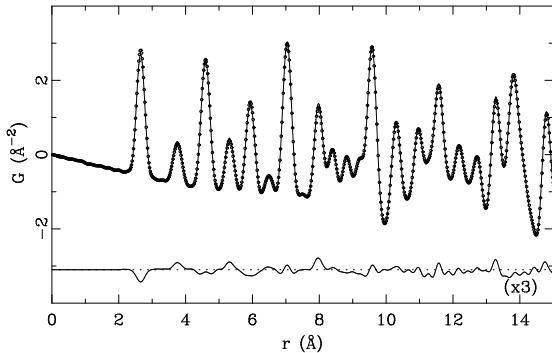


Fig. 4. Calculated PDFs of the starting (solid line) and resulting structure (circles) of Cu₃Au from the RMC refinement. The difference between both PDFs is enlarged by a factor of three and shown below the curves.

show that in our rapidly quenched Cu₃Au sample, locally there is a tendency for Cu and Au to order in a way characteristic for the fully ordered sample.

Two requirements can be identified to successfully extract SRO parameters from PDF data: First high quality data need to be obtained. The information about the SRO is only a small fraction of the PDF intensities, obviously depending on the particular scattering powers of the sample under investigation. Fig. 4 shows the difference between the calculated PDF of the starting structure of the random sample and the resulting PDF after the RMC refinement. The extracted information of the Cu-Au ordering is contained in the difference of the two. Note that the difference curve shown in Fig. 4 is magnified by a factor of three. The other important factor is to have sensible constraints when running the RMC refinement. This is discussed in much detail in the paper by Tucker et al. (2001). In this case the RMC refinement was only allowed to switch sites for copper and gold atoms. The structural parameters obtained by the refinement of a model of the average structure were kept fix. This way the only way to improve the fit was to introduce Cu-Au SRO. As a next step, we are planning to collect in-situ high temperature PDFs of Cu₃Au in order to be able to compare the extracted SRO parameters with literature values obtained from single crystal diffuse scattering data. It is clear that there are also many ways how the data refinement can be improved. In our example, the displacement parameters for the random sample were identical for copper and gold, where as they are quite different in the ordered case. One possible step forward would be to allow one to adjust site specific displacement parameters during the RMC refinement. Efforts in this direction are under way. In our previous paper (Proffen, 2000) we have also investigated cases where chemical SRO as well as local distortions are present in the sample. Our efforts now focus on finding a suitable system to demonstrate that the PDF method also works in this more complicated case.

In summary, we have demonstrated that it is possible to extract chemical SRO parameters of crystalline materials from the PDF obtained from powder diffraction data. This opens the door for rapid determination of SRO parameters as a function of external parameters such as temperature or pressure using the PDF technique.

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